I.
A PHOTOMETRIC EVALUATION OF QUENCHING OILS

II.
X-RAY STUDIES OF 2, 4 DINITROPHENYLHYDRAZINE DERIVATIVES

BY

WILBUR IRVING KAYE

B. S., J. B. Stetson University, 1942

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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URBANA, ILLINOIS

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PART I. A PHOTOMETRIC EVALUATION OF QUENCHING OILS

INTRODUCTION

At the request of the Delco Remy Division of the General Motors Corporation the oxidation stability of quenching oils was studied. It has been found that the strain induced in aluminum airplane castings on quenching in oil greatly increased with ageing of the quenching oil. These castings of aluminum alloy were quenched rapidly from a temperature of 480° C. (900° F.) in a quenching oil maintained at approximately 45° C. This hot quenching of the metal oxidized the oil producing a byproduct which in some manner impaired the heat conduction properties of the oil. A study of the heat conducting properties seemed to be beyond the scope of the equipment immediately available for use; however, it was highly desirable to devise some method of studying and evaluating the oxidation stability of various oils so that the one of highest quality might be selected with assurance of optimum performance and life in 5000 gallon lots. The method chosen was one based on spectophotometric absorption values of the oils at different stagese of use.

EXPERIMENTAL RESULTS

Spectrophotometric curves, plotted as ratios of the transmissions of deteriorated to original oils were found to be a valuable new method of studying the effects of dilution, additive action, catalytic effects of metal surfaces and the rate of oxidation of oils. These results parallel oxidation studies by other methods (1, 2, 3).

The ratios of transmissions, measured with a Cenco-Sheard Spectrophophotelometer, at the wave length of maximum absorption were found to be a good indication of the degree of oxidation stability of quenching oils. Comparing the relative transmission ratios of quenching oils with the strain induced in castings quenched in these oils, it was found that the in-

duced strain most closely followed the relative transmission values of the used quenching oil to this same oil after a further short heating period in the laboratory, indicating the fact that the induced strain was most likely connected with the rate of formation of oxidation products rather than the actual amount of oxidation products already present, though the presence of these products seem to catalyze the further formation of oxidation products.

The most stable and effective quenching oil judged spectrophotometrically and practically in terms of casting strain is one which has been subjected to oxidizing and quenching conditions in the presence of additives, and then filtered through activated clay (4). Subsequent oxidation of the oil is then uniformly linear with time and slowest. In these oils additives have comparatively little effect.

Electron Micrographs prove the formation of insoluble sludge particles from oxidation of unstable aromatic and naphthenic fractions of oil. These are almost completely absent only in the filtered used oil. These particles may have the largest single effect on thermal conductivity in the quenching of castings. The results of this research may be found in more detail in their published form.(5)

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PART II. X-RAY STUDIES OF 2, 4 DINITROPHENYLHYDRAZINE DERIVATIVES

INTRODUCTION

2,4 Dinitrophenylhydrazine has for some time been consid-

ered a good characterizing reagent for carbonyl compounds (1,2); however, various workers reporting in the literature have not agreed on the melting points. Since the melting point is the most widely used test of identification this is a serious objection to the use of the reagent. The use of x-ray powder patterns for the identification permits a more positive results for mixed as well as pure carbonyl compounds.

In addition to its value in the qualitative identification of the aldehyde 2, 4 dinitrophenylhydrazones, the x-ray method is applicable to the quantitative estimation of pure and mixed aldehydes and offers a method of studying the structural differences between the modifications of the 2, 4 dinitrophenylhydrazones of the same aldehyde.

EXPERIMENTAL RESULTS

The unit cell parameters and space groups have been determined for a number of aldehyde 2, 4 dinitrophenylhydrazones using Weissenberg, oscillation, rotation and powder patterns of the crystals. The results of this work are listed in Table I.

The triclinic unit cell of formaldehyde 2, 4 dinitrophenylhydrazone was confirmed from reciprocal lattice projections of the powder pattern, and the orientation of the molecule in the unit cell was proposed from considerations of the theoretical size of the molecule (3), the cleavage plane and the intensities of the interferences.

Crystalline modifications of acetaldehyde and n-butyraldehyde 2, 4 dinitrophenylhydrazone not previously classified in the literature have been found. The new acetaldehyde derivative had a melting point of 165° C. and was prepared by crystallization from n-propyl alcohol. The previously reported meta-stable form (4,5) of acetaldehyde 2, 4 dinitrophenylhydrazone was not found in samples of the fused stable form. The melting point of mixtures of the stable form and new form was not more than four degrees lower than either of the pure forms. Measurements on the density and size of the unit cell did not permit the molecular weight of the crystalline compound to include solvated molecules.

TABLE I

CRYSTALLOGRAPHIC DATA OF ALDEHYDE 2, 4 DINITROPHENYLHYDRAZONES

Compd.	System	a_o	b_o	c_o	γ	Den.	n	s.g.
Form.	triclinic	10.40	10.00	4.23	$\gamma = 87°$	1.582	2	$P_{\bar{1}}$
					$\alpha = 85°$			
					$\beta = 86°$			
Acet. (y)	tetragonal	13.69	7.14	7.15		1,541	4	$P4_2/n$
Acet. (o)	orthorhombic	17.3	10.6	5.06		1.51	4	$P2_12_1$—
Croton.	orthorhombic	18.30	13.05	4.63		1.43	4	$P2_12_1$—
n-Butyr. (y)	orthorhombic	54	17.9	4.90		1.3		
n-Butyr. (o)	orthorhombic	25.8	25.0	7.0		1.3		
Furfur. (y)	Monoclinic	11.7	7.7	3.63		95°	1	P_m
Furfur. (r)				7.85				

In the case of n-butyraldehyde 2, 4 dinitrophenylhydrazone three crystalline modifications were identified whereas the literature distinguishes only one (1,6,7) melting at 123° C. The two new forms both have melting points at 122° and the melting point upon mixing the forms is depressed no more than two degrees.

The x-ray powder method was applied to the micro qualitatives analysis of pure and mixed aldehydes by photographing the pattern of the 2, 4 dinitrophenylhydrazones. Samples of powdered derivative as small as 0.1 mg. and single crystals smaller than 1 microgram were identified. The data necessary for the identification of 9 forms of the 2, 4 dinitrophenylhydrazones of 5 different aldehydes are given.

By accurately measuring the ratios of line densities of mixtures of the 2, 4 dinitrophenylhydrazone with sodium fluoride a system of quantitative analysis of pure and mixed aldehydes was presented. In fundamental work on NaCl-KCl mixtures an accuracy better than 3% was achieved; however, the accuracy of analysis of mixed aldehydes was believed limited to 5%.

A method of studying the structures of closely related compounds was believed to follow from the quantitative data. By the use of an internal standard, intensities of interferences from different compounds could be compared. The strong outer spacing of the 2, 4 dinitrophenylhydrazone was believed to occur from planes in the unit cells parallel to the plane of the benzene ring of the molecule and separated by a distance equal to the thickness of the molecule. Hence by comparing intensities proportional to the absolute value of the line intensities some indication of the "degree of planarity" and thickness of the molecule could be determined.

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VITA

The author was born in Pelham Manor, New York, January 28, 1922. His primary education was received in the public schools of Pelham Manor and Lake Helen, Florida. His secondary education was completed in the high school of DeLand, Florida, in 1939. He entered J. B. Stetson University in the summer of 1939 and received the Bachelor of Science degree in June 1942. He attended the graduate school of the University of Illinois from July 1942 to January 1945. He held a teaching fellowship during the winter semesters of 1942-43 and 1943-44. During the summer semester of 1943 he held an industrial fellowship with the National Lead Company. Beginning June 1944, he was special research assistant working on Penicillin under contract OEM cmr 439. He married Virginia Agett on February 7, 1944. The author is a member of the following: American Chemical Society, Sigma Xi, Gamma Sigma Epsilon, and Sigma Pi Sigma.